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(Under International Convention.)

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Date of Application (in the United Kingdom), 21st June, 1911

At the expiration of twelve months from the date of the first Foreign Application, the provision of Section 91 (3) (a) of the Patents and Designs Act, 1907, as to inspection of Specification, became operative

Accepted, 9th Nov., 1911

COMPLETE SPECIFICATION.

Method of Making Betulin suitable for the Production of Coating Compositions.

I, JOHAN ROBERT KÖHLER, of 58, Freygatan, Stockholm, Sweden, Lecturer and Chemical Engineer, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

5 This invention relates to a process of making betulin suitable for the production of coating compositions.

10 In the manufacture of coating compositions of betulin as a substitute for usual lac-varnishes and the like certain difficulties arise which are due partly to the slight solubility of the betulin in cold solvents, partly to the tendency of the betulin to crystallise when the solvent is removed.

Pure betulin produced in the usual manner is dissolved only to a comparatively small degree in cold solvents such as alcohol, while the solubility is increased essentially in heated solvents, but when the latter are cooled the excess of the dissolved betulin again crystallises, and for this reason it is not possible
15 in this way to produce coating compositions containing betulin as an ingredient.

If the betulin be melted it again becomes crystalline when solidifying on cooling. The melting point of such betulin as well as the solubility conditions are the same as those of betulin which has not been melted.

20 I have now found that it is possible by heating the betulin somewhat above the melting point of the same (253° C) for a sufficient length of time to remove its tendency to crystallise, the molten mass in such case when being cooled becoming hard, glassy and transparent. This product is however still not suitable as a coating composition, since it is still difficult to dissolve; the melting point is inconsiderably lower than that of the original betulin. By heating the betulin

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considerably above its melting point for a sufficient length of time it is possible to increase its solubility to such an extent that it can be used for the above mentioned purpose. Betulin treated in this manner does not crystallize from a concentrated heated solution when the latter is cooled, and the solution has properties which make it quite equal to a good lac-varnish, inasmuch as the betulin when the solvent is dried or removed becomes solid and forms a hard mass of glassy structure. 5

The heating of the betulin used according to the present invention is varied according as the betulin is heated alone or in solution and also according to the length of the time of heating. If the betulin is heated alone, the temperature must be raised considerably above the melting point (about 50—120° C. above the melting point), and, as the betulin rapidly assumes a dark colour when heated to such a high temperature in air on account of partial decomposition, the heating should take place either in a vacuum or in an inert gas atmosphere. The time of heating may be varied from one to twenty hours depending on the temperature used, a higher temperature rendering it possible within certain limits to heat for a shorter time. Any exact limits for temperature and time of heating cannot, however, be given, inasmuch as such limits depend on the quantity treated, the degree of purity of the betulin, the stirring of the molten mass, the pressure used and so on. Generally the temperature and the time of heating therefore must be determined empirically in each special case. The object of the heating is obtained when the mass is rather easily dissolved in hot turpentine oil and when from a concentrated solution no precipitation takes place on the solution being cooled. The melting point of the mass is generally about 130—140° C. and cold solutions of the same may be produced containing up to 50% of betulin or more, while hardly one *per cent.* of the usual crystallized or melted betulin is dissolved in cold solvents. 10 15 20 25

The cause of the change in the betulin during heating in accordance with the present invention has not yet been ascertained. Probably an inner re-construction of the betulin molecule takes place as is the case with the natural resin acids, which, when heated, are transformed into isomeric colophon acids having quite other properties than the original acids as to their relation to polarized light, their solubility, melting point and so on. 30

The melting point generally falls the lower the higher the temperature used and the longer the time during which the betulin is heated. If the heating is continued too long or at too high a temperature the betulin may be transformed into a half solid, sticky, non-drying mass. 35

EXPERIMENT 1.

Betulin was heated in a vacuum of 20 to 30 m.m. mercury pressure with and without admitting a current of an inert gas, for instance carbonic acid (CO₂), for the purpose of stirring. Good results were obtained by using a temperature of 350 to 370° C. and a time of heating of about four hours. A lower temperature (300 to 320° C.) and a longer time generally gave the same result. The melting point of the final product was about 140° C. Good lac-varnishes could be manufactured of the same while using well known solvents, such as linseed oil, turpentine oil, acetone and so on. 40 45

EXPERIMENT 2.

Betulin was heated at the usual pressure in an atmosphere of CO₂. Good results were obtained by using a temperature of 350 to 370° C. and a heating time of about four hours. The product obtained was similar to that described under experiment 1 but was of a somewhat darker colour. 50

EXPERIMENT 3.

Betulin was heated under pressure in an atmosphere of CO₂. A soluble product with a melting point of 130 to 135° C. was obtained by using a temperature

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of 360 to 370° C. and a time of heating of about three hours. At a higher temperature (for instance 400° C.) decomposition took place and the product became dark brown. Also heating continued too long proved unfavourable. Thus the betulin heated during five hours to 365° C. was transformed into a yellow-brown, half solid, non-drying mass. Heating to a lower temperature than 360° C. during a longer time resulted in an amorphous, glassy mass, which was difficult to dissolve and therefore could not be used for the present purpose. Thus at a temperature of 340° C. and a time of heating of fifteen hours an insoluble product was obtained. The latter had a melting point of 232° C.

Instead of heating the betulin alone, as described above, one may accomplish the transformation by absorbing it successively in a hot solvent, for instance linseed oil, or turpentine oil, or a mixture of these oils under pressure.

Betulin in its natural state is difficult to dissolve in linseed and turpentine oil for which reason it precipitates in a crystalline or amorphous state from hot solutions of the usual betulin in linseed or turpentine oil when the solutions are cooled. If however the betulin is dissolved in the solvent by heating the latter under pressure to temperatures above the melting point of the betulin, a lac will be obtained which may contain 50% of betulin or more, and the betulin does not precipitate from the solution when the latter is cooled. Clear solutions of crystallized betulin in linseed oil (or turpentine oil) have been obtained at a temperature of 255—280° C. and a time varying between 30 minutes and 5 hours. With the shorter time solutions containing about 20% of betulin were obtained, while with longer heating the solutions contained about 50% of betulin. Betulin extracted from the last mentioned solutions has a melting point of about 190—195° C.

To make betulin suitable for the production of coating compositions one may use a combination of the above described two methods in such manner that the betulin is first melted and heated alone above its melting point but to a lower temperature or for a shorter time than is required for complete transformation of the same, whereupon the product thus obtained is dissolved in a suitable solvent which is heated to such a high temperature and during such a period of time that complete transformation of the betulin takes place. This combined method is to be preferred when the invention is to be carried into practice on a large scale, since it is possible to use comparatively low temperatures and the product obtained in this manner as a rule becomes more colourless than otherwise. Also in this case the temperature and the time of heating must be determined empirically.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process of making betulin suitable for the production of coating compositions consisting in heating the betulin alone or in a suitable solvent to a temperature above its melting point for such a length of time that it does not precipitate from a hot concentrated solution when the latter is cooled, and that when the solvent becomes dry or is removed, it grows solid and forms a body of a hard glassy structure.

2. Process as set forth in Claim 1, consisting in heating the betulin at a higher or lower pressure than that of the atmosphere.

3. Process as set forth in Claims 1 or 2 consisting in heating betulin in an inert gas atmosphere.

4. A modification of the process set forth in Claim 1 consisting in first heating the betulin alone to a temperature above its melting point to effect a partial transformation of the same, dissolving the product obtained in suitable solvents at such a high temperature and for such a length of time that the betulin does not precipitate from a hot concentrated solution when the latter is cooled, and

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that when the solvent becomes dry or is removed, it grows solid and forms a body of a hard glassy structure.

Dated this 21st day of June, 1911.

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